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ACID AEROSOL TRANSPORT EPISODES IN TORONTO, ONTARIO

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16. ABSTRACT

Authors used recently developed equipment to continuously monitor levels of H_2SO_4, NH_4HSO_4 and $(NH_4)_2SO_4$ concentrations in the ambient air outside Toronto, Ontario. These data were combined with 48-hour isobaric air mass back-trajectories ending in Toronto on each of the four days with highest acid(and sulfate) aerosol levels. The air masses with highest acid levels were found to have first passed over the SO_2 source region of the U.S. and then across the Great Lakes to Toronto. The role of ammonia as a modulator of aerosol acidity for eastern U.S. cities but not for Toronto (where the Great Lakes serve as ammonia sinks) is also discussed.

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INTRODUCTION

During July and August of 1986, New York University and the U.M.D.N.J. - Robert Wood Johnson Medical School, in cooperation with the Ontario Ministry of the Environment, conducted a field survey of acidic air pollution levels in the Toronto, Ontario metropolitan area. Of special interest was a determination of the ambient levels of particulate hydrogen ion (H^+), as well as an assessment of the chemical form in which this acidic aerosol is present. This determination was made possible through the use of a reliable continuous total sulfate/sulfuric acid aerosol monitor deployed in conjunction with a sampler for total particulate hydrogen ion concentration.

The rationale for this research, conducted as part of a cooperative agreement with the U.S. EPA, was based in part on the findings of Bates and Sizto (1,2), who have reported associations between elevated sulfate levels and hospital admissions for respiratory causes in Southern Ontario. In their original study (1), a significant correlation ($p < 0.001$) was found between acute hospital admissions for respiratory disease and daily O_3 and SO_2 concentration and ambient temperature, and with 24 and 48 h lags of the environmental data. In the subsequent study (2), using a limited body of available sixth day 24 h sulfate (SO_4^{2-}) ion data, SO_4^{2-} was found to be the index most highly correlated with asthma admissions. However, our hypothesis is that SO_4^{2-} was probably only a surrogate for the acidic sulfate components within it, since the relationship observed was more statistically significant than that of irritants, such as ozone and sulfur dioxide, known to be more potent irritants than ammonium sulfate, which is the SO_4^{2-} species most often present in the highest concentration. Ammonium sulfate would be unlikely to produce respiratory responses even at concentrations up to 45 $\mu g/m^3$, the highest total SO_4^{2-} observed. Thus, it is thought that comparisons of the hospital admissions data with exposure to H^+ and/or H_2SO_4 should yield a stronger dose response relationship. Ultimately, it is our objective to correlate the acid aerosol data presented in this paper with hospital admissions records to assess the role of acid aerosols in the incidence of Toronto's respiratory admissions.

Air pollution epidemiology through the 1950's and 1960's was able to demonstrate instances where increases in daily mortality or morbidity in London, England, were associated with elevated concentrations of index air pollutants, i.e., smoke and sulfur dioxide. However, subsequent analyses suggested that these pollutants were surrogates for a more active component, i.e., acid aerosols. The only known field epidemiologic investigation in which sulfuric acid (H_2SO_4) was measured directly and was implicated as the causative agent for human health effects occurred in Yokkaichi, Japan, in the 1960's (3). During a period of about 8 years, when there were high emissions of H_2SO_4 mists from a titanium dioxide pigment plant, there were an excess of 600 cases of respiratory morbidity in downwind populations. Unfortunately, the actual H_2SO_4 concentration data were severely limited, and most inferences of exposure were obtained from litmus paper measurements collected at various locations in the residential district around the plant.

In view of these and various other studies, Lippmann (4) speculated that the active agent, and the pollutant with potentially the highest level of health significance, would be the hydrogen ion concentration (H^+). The SO_4^{2-} ion is thought to be only an indicator of the presence of irritant species, since it represents the sum of the concentrations of various forms: H_2SO_4, $(NH_4)HSO_4$ and $(NH_4)_2SO_4$. Past studies conducted at New York University's Institute of Environmental Medicine and other laboratories indicate that the distribution of these chemical species within the total sulfate is highly variable in the atmosphere (5,6,7).

In this paper, we examine the pollution data collected during the July and August 1986 field study in order to assess the nature and sources of acidic aerosols in the Toronto metropolitan area during this period. Through the examination of the continuous and filter aerosol data, isobaric back-trajectories of air masses, weather maps, and available trace element data, assessments are made of the character and possible sources of acid aerosols in this Southern Ontario city.

Data Collection

A continuous sulfate/sulfuric acid monitor was operated from July 3 through August 10, 1986 at a monitoring site on the University of Toronto Scarborough Campus, located within the Toronto metropolitan area, approximately 20 km northeast of downtown Toronto. The total sulfate/sulfuric acid aerosol monitor presently being employed by NYU represents the culmination of a series of researchers' efforts to develop a reliable instrument suitable for continuous long-term field observations (8,9,10). In brief, the instrument utilizes a Flame Photometric Detector (FPD) to measure the sulfur in the sampled air entering it, preceded in the sampling train by a lead oxide (PbO) coated gaseous sulfur denuder, which is itself preceded by a thermal ramp capable of raising the air sample's temperature prior to the denuder and FPD (see Figure 1).

The result of this sampling configuration is to allow a discrimination of total particulate sulfate into its chemical components via a cyclical operation of the thermal ramp at preset temperatures. The unit is first operated for 3 minutes at ambient temperature, and the denuder removes any gaseous sulfur (i.e., sulfur dioxide, SO_2) prior to the FPD, yielding the total particulate sulfur level. The thermal ramp is then used to heat the upstream sampled air to 120°C for 3 minutes, volatilizing any H_2SO_4 in the air, causing that H_2SO_4 to also be removed by the denuder, and resulting in a concomitant drop in the recorded particulate sulfur. Similarly, raising the thermal ramp to 300°C for 3 minutes causes any ammonium sulfate ($(NH_4)_2SO_4$) or ammonium bisulfate (NH_4HSO_4) to be volatilized and removed by the denuder, as well. Finally, purified (zero) air is fed through the system to provide a reference point for determining the absolute quantity of each type of sulfate. By differencing the respective 3 minute values over the 12 minute cycle (which is repeated five times per hour), this instrument provides near real-time measurements of total particulate sulfates, ammonium salts, and H_2SO_4.

Unfortunately, the sulfate acid aerosol monitor cannot discriminate between NH_4HSO_4 and $(NH_4)_2SO_4$ on the basis of temperature of volatilization alone. Because of this, the monitor is accompanied by a dichotomous size selective particle sampler ($d_a < 2.5$ μm) in order to collect the total hydrogen ion (H^+) concentration in the air on Teflon filters. Integrating the H_2SO_4 concentration from the continuous acid aerosol analyzer over the H^+ sample period, the H^+ associated with the H_2SO_4 can be subtracted from the total, and the ammonium bisulfate concentration can be inferred. In this manner, the parallel use of a size selective aerosol monitor and the total sulfate/sulfuric acid aerosol monitor allows individual determinations of the H_2SO_4, NH_4HSO_4 and $(NH_4)_2SO_4$ concentrations on a routine basis.

The aerosol filter collection and analyses steps employed in this research are summarized in Figure 2. Numerous quality assurance procedures were employed to ensure that H^+ concentrations were accurately measured. As noted in Figure 2, samples were protected from neutralization by ambient ammonia gas both before and after sampling. In addition, the samples analyzed were of the fine mass fraction ($d_a < 2.5$ μm) which avoids possible on-filter neutralization by alkaline coarse particles. Upstream annular denuders (periodically recoated with citric acid) were employed to remove ammonia gas from the air stream prior to the sample. Proper filter blanks and pre-dosed hydrogen ion control samples were also included in our regular sampling regime in order to ensure the adequacy of our quality assurance steps.

In addition to the continuous sulfate/sulfuric acid monitor and acid aerosol filter data collected simultaneously at the Scarborough Campus site, other pollution variables were collected at this site and at other sites in the metropolitan area. Other pollutants measured at the Scarborough Campus included ozone, sulfur dioxide, and nitrogen oxides. In addition, acid aerosol filter data were collected at two other metropolitan Toronto sites at times concurrent with the Scarborough Campus samples. These two sites were the Ontario Ministry of the Environment (MOE) labs at Resources Road in northwestern Toronto and the MOE downtown Toronto site at Breadalbane Street. In addition, ozone data were collected at each of these two sites, as well as at the MOE monitoring site at Kennedy and Lawrence Avenues, located between downtown Toronto and the Scarborough Campus. At the Breadalbane site, daily dichotomous samples (midnight to midnight) were collected for subsequent analysis by x-ray fluorescence (XRF) for trace elements, including sulfur and selenium.

With regard to meteorological data, continuous on-site surface wind speed and direction, temperature, and relative humidity data were collected at the Scarborough Campus site. Wind speed and direction data at 75 and 250 ft elevations were also collected at the Kennedy and Lawrence Avenue MOE site. Surface 48-hour isobaric air mass back-trajectories were also provided by the Canadian government's Atmospheric Environment Service (AES). AES also made select satellite photographs available to NYU to aid in our interpretation of the meteorological data.

RESULTS

Concentrations of key air pollution variables collected during the Toronto field study are summarized in Figure 3. The H^+ and SO_4^{2-} data are daytime filter values (9 AM - 5 PM) for each day as measured at the Scarborough Campus site. The fine particle Se and mass (FPM) concentrations displayed are 24-hour averages for each day from the Breadalbane site. The maximum O_3 values are those recorded at the Kennedy and Lawrence site. Four relatively high acid aerosol days (all $\geq$ 75 neq/m^3 H^+, or 3.7 $\mu g/m^3$, if as H_2SO_4) are readily identified in Figure 3: day 187 (July 6), day 200 (July 19), day 206 (July 25) and day 220 (August 8). These high acid aerosol days are also notable as elevated ozone and total $SO_4^=$ days, as well.

Figure 4 presents the 48-hour isobaric air mass back-trajectories ending in Toronto at 18Z (1 PM EST) on each of the four highest acid (and sulfate) aerosols days. Clearly, it is air masses which have first passed over the SO_2 source region of the U.S. and then across the Great Lakes to Toronto which are associated with the highest sulfate and acid aerosol days occurring during this field study. It is interesting to note, however, that these four days are not always indicated as the highest Se concentration days (See Figure 3), even though July 25th, the maximum SO_4^{2-} and H^+ day, is also the highest Se day. Indeed, a moderate Se peak occurs on Day 209 (July 28), a day for which the 48 hr trajectory (not shown) passed only over Eastern Canada, perhaps suggesting that Canadian sources may be responsible for this modest peak in Toronto. This is in contrast to Eastern U.S. locations, where the Se tracer has been reported to be primarily associated with coal combustion (11). The location of this site between U.S. and Canadian sources of SO_2 and Se may confound the use of Se as a unique tracer in Toronto, and additional analyses (e.g., for As) may well be required if trace elements are to be used as reliable sole indicators of acid aerosol source region at this site. On July 25, 1986, however, the trajectory data strongly imply that the maximum Se, H^+, and SO_4^{2-} concentrations recorded are contributed to by pollution of U.S. origins.

Figure 5 displays more detailed sulfate/acid aerosol information for July 25, 1986. H_2SO_4 only occurs during a brief portion of this sulfate episode, and the H_2SO_4 concentration data averaged over the coincident filter sampling periods indicates that only about 6 percent (e.g., 0.8/13.8) of the acidity is actually in the form of H_2SO_4. For both periods, the majority of the acidity (and indeed of the $SO_4^=$) is calculated as being in the form of NH_4HSO_4. This is indicative of a moderately aged acid aerosol air mass, wherein the H_2SO_4 originally formed or emitted has been partially neutralized to NH_4HSO_4. The remaining SO_4^{2-} (mostly $(NH_4)_2SO_4$) makes up only about 35-45 percent of the total SO_4^{2-} during this acid aerosol event. All of the major acid aerosol events during this study were found to have similarly low H_2SO_4 values (relative to total acidity), implying the dominance of NH_4HSO_4 during acid aerosol events at this location.

DISCUSSION

In eastern North America, fine acidic aerosols are often dominated by sulfates, both in terms of mass and hydrogen ion contribution. These sulfates are most commonly found as sulfuric acid (H_2SO_4), ammonium bisulfate (NH_4HSO_4) or ammonia sulfate ($(NH_4)_2SO_4$). At 50% relative humidity, H_2SO_4 is the most strongly acidic sulfate form (pH < 1.0), while ammonium bisulfate is roughly half as acidic (pH = 1-2) and ammonium bisulfate is very weakly acidic (pH > 5.0) (12). Thus, ambient sulfates may range from very acidic to only weakly acidic, depending on the proportion of the sulfate present in each of these differing species.

The acidity of an aerosol high in sulfates is dependent upon how much neutralization has occurred since it was formed in or released into the atmosphere. Although ambient sulfate chemistry is complex, potentially involving both gaseous and liquid phase reactions, it can be qualitatively characterized as involving the initial formation or emission of sulfate as H_2SO_4, followed by its neutralization first to NH_4HSO_4, and then to $(NH_4)_2SO_4$. The acidity of ambient aerosols, then, are largely a function of the rate at which H_2SO_4 is being added (by either primary emissions or atmospheric formation via oxidation of SO_2) and the rate at which neutralizing reactions with dissolved ammonia gas (which is extremely soluble in acidified droplets) can convert that H_2SO_4 to a more neutral sulfate species.

Ammonia (NH_3) is the predominant basic gas in the atmosphere and, as such, its concentration in the atmosphere is a major determinant of aerosol acidity (13). Over 99 percent of the Earth's atmospheric ammonia is produced by biogenic sources, the main source being the decomposition of organic waste. However, in urban areas, anthropogenic sources may locally increase gaseous ammonia levels. Anthropogenic sources of NH_3 include combustion processes (such a municipal incineration and automotive emissions) and industrial sources (such as fertilizer factories and petroleum refineries). Atmospheric losses of annhydrous ammonia fertilizers and ammonia from cattle feedlots are also sources of ammonia. Aside from reaction with atmospheric acids, major sinks of ammonia include plant absorption and absorption by bodies of water. In general, ambient measurements of ammonia gases indicate that the highest ammonia gas concentrations are recorded in major urban areas, the lowest over large water bodies, and intermediate levels in rural areas (13).

In light of these discussions, the Toronto acid aerosol episodes can be better understood. As displayed in Figure 4, the highest H^+ concentration air masses had passed over an area rich in SO_2 emissions (e.g., the Ohio River Valley region), followed by passage over the Great Lakes, which lack in ammonia sources and, indeed, may act as a gaseous ammonia sink. An example weather map for July 25th, displayed in Figure 6, also supports the isobaric trajectory results, indicating airflow from the U.S. across the Great Lakes on this day. Thus, it would appear that such air masses entering Toronto can be very acidic because they carry with them high levels of H_2SO_4 formation precursors, probably combined with low levels of neutralizing ammonia gas over the Great Lakes.

This contrasts with urban New York City, for example, where acid laden air masses from the west must first pass over substantial ammonia sources in both agricultural western New Jersey and industrial and urbanized eastern New Jersey. Interestingly, the Toronto acid aerosol results are also in sharp contrast to summertime acid aerosol results from New York City, where (despite elevated upwind acid aerosol concentrations) urban sulfates were consistently found to be in a completely neutralized state (14). Thus, the presence of relatively elevated acid aerosol concentrations in metropolitan Toronto is consistent with the chemistry and meteorology thought to be associated with sulfate episodes in this city.

The hypothesis that the acid aerosols recorded at the Scarborough Campus site are due to a regional scale sulfate transport event is supported by contemporaneous data available from other sites in Southern Ontario. First, H^+ measurements at our other two Toronto sites (although not reported in this paper) do confirm that, when elevated acidity and sulfates were recorded at the Scarborough site, elevated levels were also recorded in downtown Toronto and to the northwest of downtown (15). Furthermore, acid aerosol measurements made in Dunnville, Ontario (along Lake Erie, 100 km to the southwest of Toronto) as part of the Canadian Federal government's Children's Acute Respiratory Effects Study (CARES) during this same period confirm the widespread nature of these episodes and appear to support our hypothesis regarding the chemistry involved. On July 25, 1986, for example, similar continuous sulfate/sulfuric acid monitoring (conducted by Harvard University for CARES) at Dunnville indicated that sulfate levels exceeded those recorded at Toronto and that approximately half of the sulfates were in the form of H_2SO_4 (16). Thus, the site to the southwest (i.e., closer to the upwind SO_2 sources) also had elevated sulfates, but those sulfates were, as would be expected, less neutralized than the aerosol measured at the downwind (and more urban) Toronto monitoring site. These independent results all support the hypothesis that this acid episode is regional in scale, and that the acidic aerosols are contributed to by upwind U.S. SO_2 sources converted to H_2SO_4 in the moist, relatively ammonia free environment over the Great Lakes, and then slowly neutralized as they pass over terrestrial Canada.

CONCLUSIONS

Results from a July and August, 1986 air pollution study in Toronto, Ontario document that acid aerosol episodes occur in this city. For example, on July 25, 1986, peak (12 minute average) sulfate concentrations exceeded 50 $\mu g/m^3$, and daytime average (9 AM - 5 PM) H^+ concentrations reached 282 neq/m^3 (13.8 $\mu g/m^3$, if as H_2SO_4). However, it was found that a majority of the acid was estimated to be as NH_4HSO_4, rather than H_2SO_4. Air mass trajectories, weather maps, and concurrent H^+ measurements at other locations indicate that regional air pollution transport across the Great Lakes from the U.S. contribute to the acid aerosol events recorded at this Toronto site.

The presence of elevated acid aerosol concentrations within the Toronto metropolitan area is contrary to past (albeit limited) experience with acid measurements in New York City, but is consistent with

both the known chemistry of acid aerosols and the geographical location of Toronto, Ontario. It is hypothesized that, as pollution passes over the Great Lakes, acid aerosols are formed but are not as readily neutralized as they would during overland transport. This fact apparently contributed to the elevated acid aerosol concentrations recorded in Toronto when polluted air masses travelled across the Great Lakes from the south and southwest.

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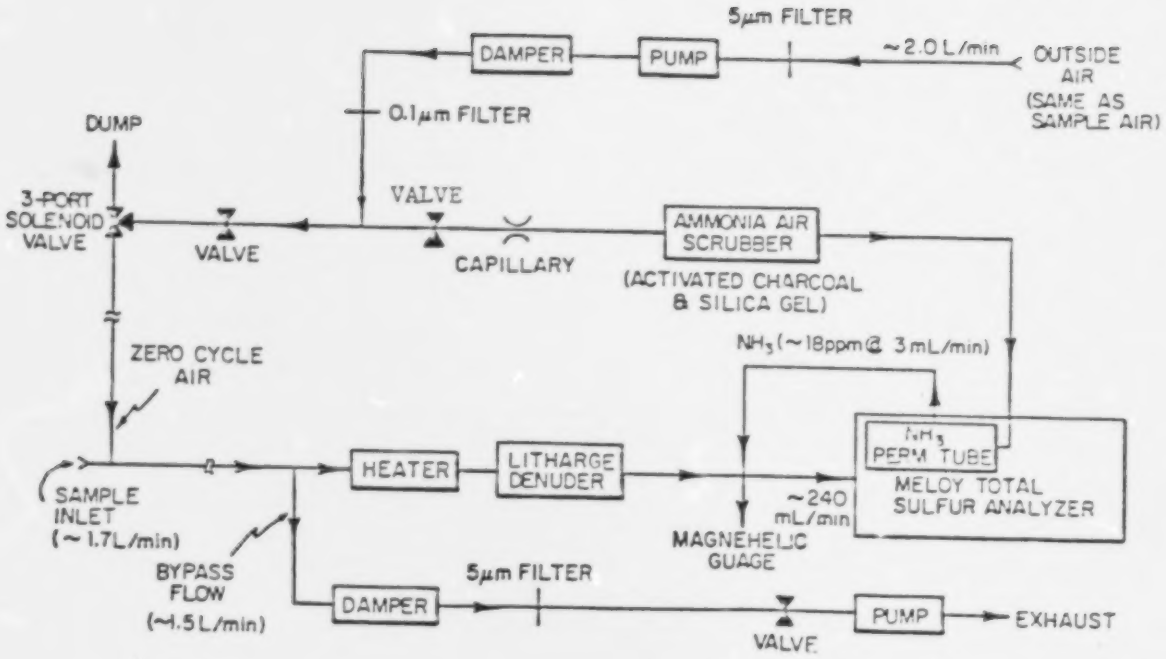


Figure 1. Flow Diagram for the Continuous Sulfuric Acid/Sulfate Monitor.

Source: Allen et al. (1984).

Figure 2. SAMPLE HANDLING & ANALYTICAL PROTOCOLS

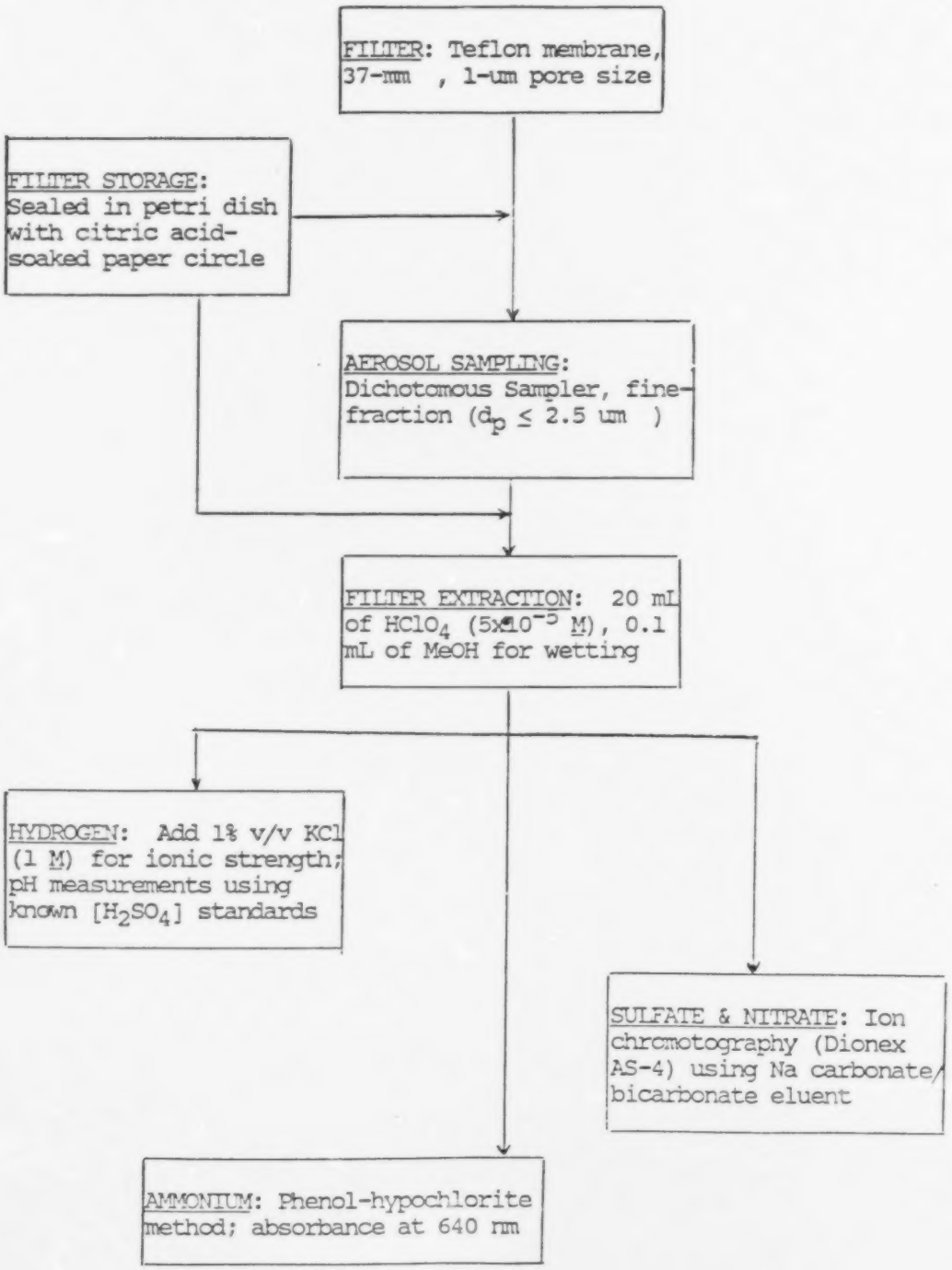
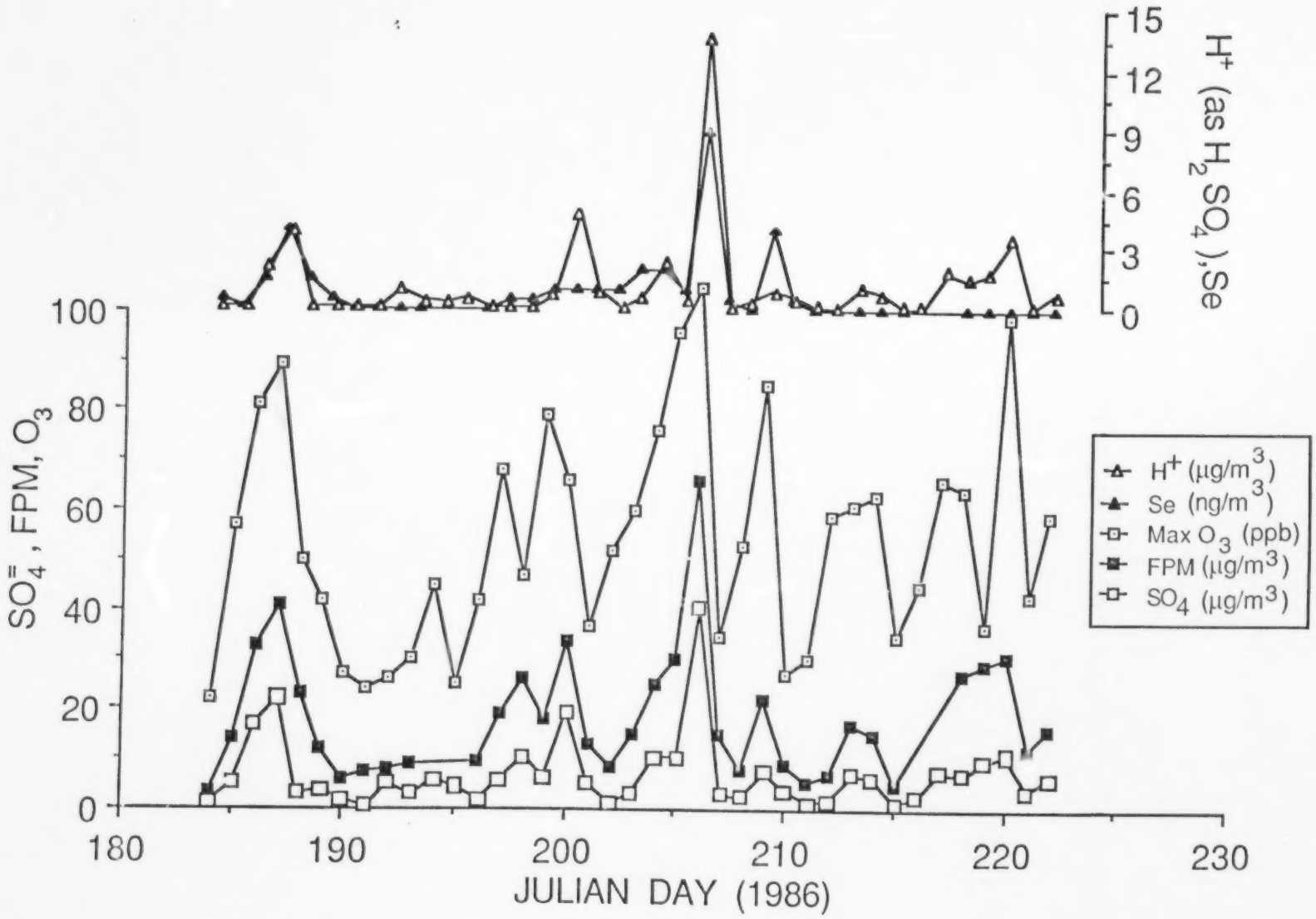

FILTER: Teflon membrane, 37-mm , 1-um pore size
FILTER STORAGE: Sealed in petri dish with citric acid-soaked paper circle
AEROSOL SAMPLING: Dichotomous Sampler, fine-fraction ($d_p \leq 2.5$ um)
FILTER EXTRACTION: 20 mL of $HClO_4$ (5×10^{-5} M), 0.1 mL of MeOH for wetting
HYDROGEN: Add 1% v/v KCl (1 M) for ionic strength; pH measurements using known [H_2SO_4] standards
SULFATE & NITRATE: Ion chromotography (Dionex AS-4) using Na carbonate/bicarbonate eluent
AMMONIUM: Phenol-hypochlorite method; absorbance at 640 nm

Figure 3. Air Pollutant Concentrations in Toronto, Ontario between July 3, 1986 (Day 184) and August 10, 1986 (Day 222)



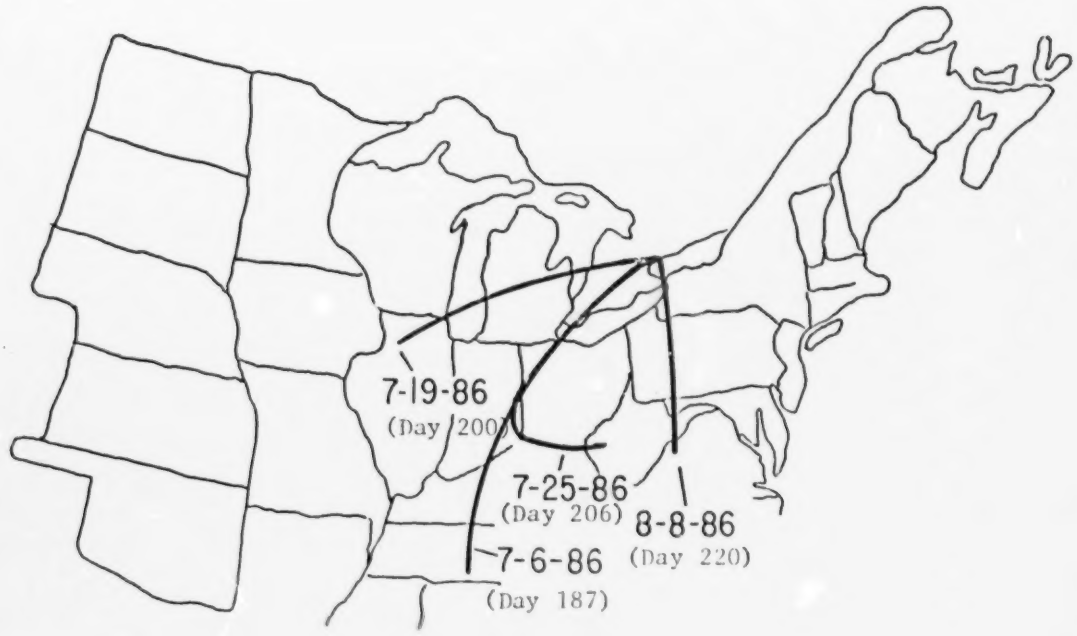
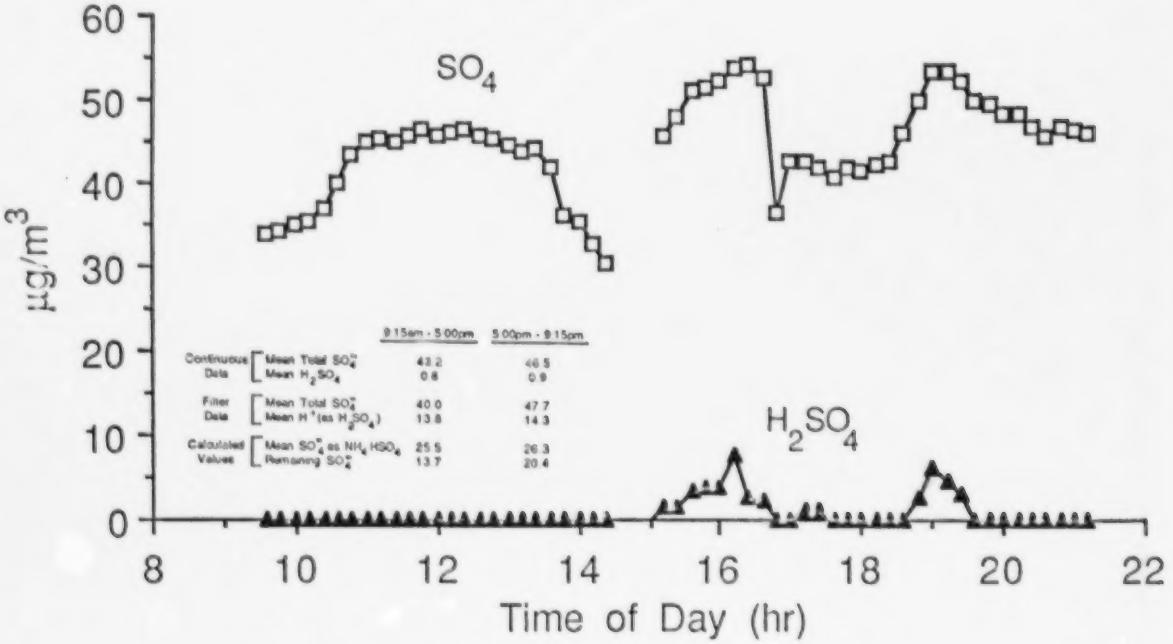


Figure 4. 48-Hour Surface Air Mass Back-Trajectories Ending on Toronto Episode Days (End time = 1 PM EST).

Figure 5. Continuous (12 minute average) $SO_4^{=}$ and H_2SO_4 Record for July 25, 1986 with Comparisons to Filter Data ($\mu g/m^3$)



FRIDAY, JULY 25, 1986

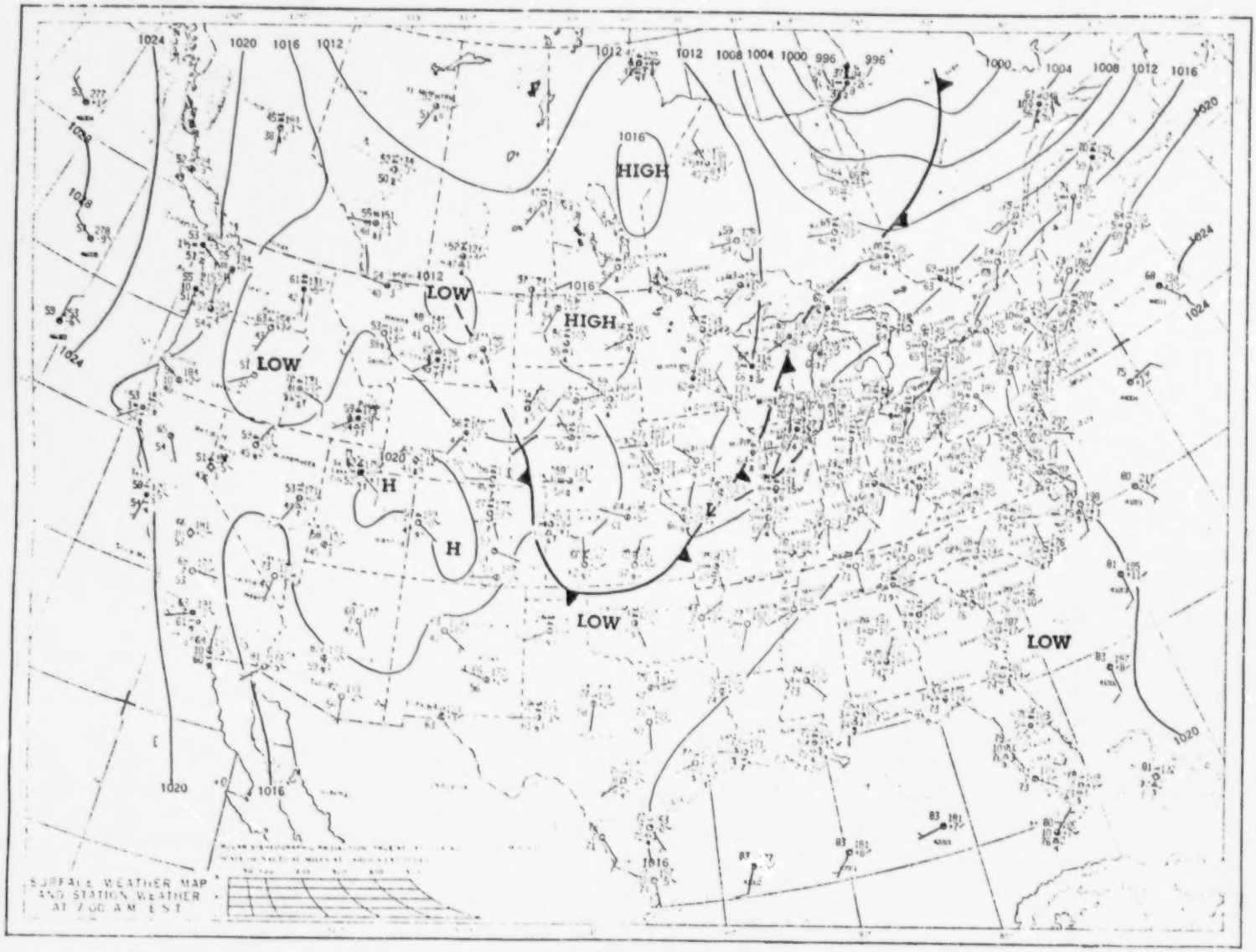


Figure 6. North American Surface Weather Map, July 25, 1986: 7 AM EST (1200Z)